Erosion of W-C Composite in Hydrogen Plasma at Temperatures Above 1000 K

Alenka Vesel, Miran Mozetič
“Jožef Stefan” Institute
Jamova 39, SI-1000 Ljubljana, Slovenia
alenka.vesel@ijs.si, miran.mozetic@ijs.si

Marianne Balat – Pichelin
CNRS-PROMES
Font Romeu-Odeillo, France

Rok Zaplotnik
Induktio d.o.o.
Litostrojska 44D, Ljubljana, Slovenia

ABSTRACT

Interaction of hydrogen plasma with W-C composite was studied. One (1) μm thick W-C composite was deposited on the polished stainless steel substrate and treated in a microwave discharge at 1000 W. The flow of hydrogen was 12 l/h and the pressure was 40 Pa. Treatment time was kept constant at 5 min. During plasma treatment additional sample heating was performed by the use of concentrated solar radiation. Temperature of the samples was varied between 1000 K and 1280 K. The temperature was measured by pyrometer. This allowed us to follow the surface chemical modification occurring during plasma treatment. A change in the chemical status of the surface caused deviation in the sample’s temperature due to changes in the sample’s emissivity. After the treatment the samples were analyzed by classical techniques for surface characterization like x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The results have shown the reduction of carbon from the C-W deposit and segregation of iron from the stainless steel substrate to the surface and formation of Fe$_7$W$_6$ intermetallic compound.

1 INTRODUCTION

Plasma facing components (PFC) of fusion devices are exposed to extreme environment. Due to intensive particle and heat loads, the surfaces of PFC materials are subjected to high material erosion, migration and re-deposition [1-4]. Especially graphite tends to be eroded by hydrogen ions during hot plasma pulses. The eroded material deposits on different walls, especially at remote parts of fusion reactors, and they represents an unpredicted source of hydrogen (in future fusion devices it will be deuterium and tritium), which has a high affinity for retention. Furthermore, these deposited layers may be subjected to further re-erosion, since hydrocarbon layers have 10-times higher chemical erosion yield than bulk graphite [5]. Therefore, the erosion and formation of re-deposited layers of hydrocarbon compounds is of major concern in the development of the next-step fusion devices [6].
At our previous experiments we have shown that hydrogen plasma can selectively remove carbon from hydrogenated carbon deposits with small amount of tungsten [7]. In the present paper we report a laboratory study on the interaction of neutral hydrogen atoms created in a microwave hydrogen plasma with C-W deposits with a ratio of 50:50 which were prepared by sputter deposition - so the worst case was chosen.

2 EXPERIMENTAL

2.1 Sample preparation

The W-C coating was prepared by reactive sputtering in a Balzers Sputron tetrode sputtering system [8-9]. The Sputron sputtering system uses the low voltage thermionic arc as a source of ions for sputtering. A plasma beam (typically 40 V/40 A) is produced between the hot filament (Ta wire) and the auxiliary anode around the target. Targets 60 mm in diameter are interchangeable in situ (up to four different materials), so we may easily produce multilayered structures. Tungsten carbide (WC) and pyrolitic graphite targets were used and the deposition was performed in Ar gas. The total pressure was $2 \times 10^{-3}$ mbar. The discharge voltage was held constant at 1700 V with 0.6 A of discharge current. During deposition a substrate temperature was kept below 120°C. The quartz crystal microbalance was used for calibration of deposition rates. Deposition rates and thickness reproducibility was better than 2%. The deposition rate was about 9 nm/min for WC.

Figure 1 illustrates the typical structure of the deposited W-C coating. Coatings were sputter deposited onto polished stainless steel substrates. A thin Cr intermediate layer was used for better adhesion between stainless steel substrate and a W-C deposit.

![Figure 1: Schematic of the sample structure (not to scale)](image)

2.2 Plasma treatment

The samples were treated in the plasma system of the MESOX set-up device which is schematically shown in Figure 2. The system was pumped with a two-stage oil rotary pump with the pumping speed of 33 m$^3$/h. The flow of hydrogen through the system was adjusted with a volume flow controller, and the pressure was measured with an absolute vacuum gauge. At our experiments, the hydrogen flow was adjusted to 12 l/h which gave a pressure of 40 Pa. The density of hydrogen atoms as measured by a fiber-optic catalytic probe was about $2.4 \times 10^{21} \times m^{-3}$ and a degree of dissociation was 19% [10]. The experimental chamber was a quartz cylinder with a length of 50 cm and an outer diameter of 5 cm. Plasma was created within a microwave cavity at 2.45 GHz and at a power of 1000 W. Other details of experimental set-up can be found in ref [10]. There was a movable quartz sample holder inside the quartz tube allowing for precise sample positioning. The samples were placed on the top of the holder as shown in Figure 2. During plasma treatment additional sample heating was performed by the use of concentrated solar radiation. The sample’s temperature which was measured by a pyrometer was varied between 1000 K and 1280 K. A treatment time was kept constant at 5 min.
2.3 Surface characterization

The chemical composition of the sample before and after plasma treatment was determined using Auger electron spectroscopy (AES) and X-ray diffraction (XRD).

The composition of the samples was determined by AES depth profiling. We used a Scanning Auger Microprobe (Physical Electronics Ind. SAM 545 A). Samples were excited with a static primary electron beam with the energy of 3 keV, the beam current of 2 µA and the diameter of about 40 µm. The electron incidence angle with respect to the normal to the average surface plain was 30°. The samples were ion sputtered with two symmetrically inclined beams of 3 keV Ar⁺ ions, rastered on a surface area larger than 6 x 6 mm at an incidence angle of 47°. The sputtering rate as determined on a C/WC/W/Si multilayer standard was about 3 nm/min. Concentration profiles were evaluated by using relative sensitivity factors from the manufacturer’s handbook. The Auger peak-to-peak heights of C(272 eV), O (510 eV), Fe (703 eV), Cr (529 eV) and W (179 eV) were measured. The following sensitivity factors were used: C (0.18), O (0.50), Fe (0.21), Cr (0.34) and W (0.113).

XRD analyses were performed using a Philipps PW1820 diffractometer. The X-ray diffraction measurements were made in the range 15°–90°. The step size and the time per step were fixed at 0.01 and 1 s. Crystalline phases were identified by comparison with standard reference patterns. The XRD diffractograms were recorded before and after plasma treatment.

3 RESULTS AND DISCUSSION

In Figure 3a is shown AES depth profile of as-deposited sample. It can be observed that carbon and tungsten are approximately in equal amounts of about 50:50. The layer is uniform and its thickness is about 1 µm. AES diagram of plasma treated sample which was heated to about 1000 K is shown in Figures 3b, while the one heated to 1280 K is shown in Figure 3c. The sample which was heated to only 1000 K looks similar as the untreated sample. The only difference is the slight reduction of carbon at the interface between the deposit and the bulk. Interesting results were obtained with the sample which was exposed to about 1280 K. This sample looks completely different. The layer now consists of about 60% of W and about 30% of Fe, while carbon almost disappeared (only few percent remained).
Figure 3: AES depth profiles of WC samples: (a) untreated, (b) treated 5 min in H$_2$ plasma at 1000 K and (c) treated at 1280 K.

Here we should mention that additional heating with solar radiation was started about 1 min after turning on plasma. After 1 min the shutters for controlling the flux of solar radiation were open to maximum to allow fast heating of the sample. After the sample’s temperature reach the desired value the temperature was kept constant by precise controlling the opening of the shutters. The temperature was measured by pyrometer. This allowed following the surface chemical modification during plasma treatment. A change in the
chemical status of the surface can cause deviation in the sample’s temperature due to changes in the sample’s emissivity (this change can not be attributed to changes in the sample’s temperature since the solar flux was kept constant). This can be observed in Figure 4b for a sample heated to 1280 K. A remarkable drop of temperature of the sample was observed after about 230 s. This temperature drop was not observed for the sample heated to only 1000 K (Figure 4a). This is in agreement with AES results. A temperature drop was observed only for the sample heated to higher temperature where segregation of iron appeared. A temperature drop probably indicates disappearance of carbon and formation of Fe-W bimetallic composite. In the case of sample heated to only 1000 K, the temperature was probably to low to cause to surface rearrangement.

Figure 4: A temperature variation of the sample which was heated to 1280 K during treatment in H$_2$ plasma.

To find out more about chemical changes of plasma treated samples we performed XRD analysis. The result is shown in Figure 5. As-deposited sample is amorphous – we observe only one very broad peak. A plasma-treated sample which was heated to only 1000 K already show indications of some changes. In XRD spectrum of plasma treated sample heated to 1280 K we can observe appearance of new peaks, while amorphous phase that was observed for the untreated sample has disappeared. New peaks were attributed to formation of Fe$_7$W$_6$ intermetallic compound. As shown on the phase diagram in Figure 6, Fe$_7$W$_6$ can be formed only above 1200 K as in our case.
Here we can conclude that in the real case, exposure of C-W coating deposited on the stainless steel walls of plasma reactors to hydrogen plasma at temperature above 1200 K can lead to formation of bimetallic compounds. Carbon can be successfully removed, but finally a layer of Fe$_7$W$_6$ is formed on the stainless steel substrate.

![Figure 5: Comparison of XRD spectra of reference WC sample and WC samples treated in H$_2$ plasma and sun for 5 min. New peaks are observed and amorphous phase disappeared.](image)

At the end we should also note that the carbon erosion rate depends on the carbon-tungsten ratio and the presence of hydrogen in the deposits. At our previous results performed with hydrogenated carbon-tungsten deposits with a lower tungsten content (below 30 at.%) we have found that carbon was selectively removed already at low temperature of about

![Figure 6: The Fe-W binary phase diagram [11](image)
850 K (the sample was heated to this temperature by plasma itself) [7]. The remained layer was only pure tungsten.

4 CONCLUSIONS

Interaction of hydrogen plasma with W-C composite was studied. W-C composite with a ratio 50:50 was prepared by sputter deposition. A sample was exposed to hydrogen plasma for 5 min at elevated temperature. The results have shown that after certain temperature carbon was selectively removed from the composite. Iron from the substrate segregated to the surface and binary $\text{Fe}_7\text{W}_6$ intermetallic compound was formed. It can be concluded that hydrogen plasma can remove carbon from the carbon-metal deposits, but on the other hand high temperatures can cause interaction of iron from reactor walls with tungsten residues from the deposits.

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REFERENCES


